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Model-based analysis of water management in alkaline direct methanol fuel cells

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HIGHLIGHTS

- First modelling study of water management in anion exchange membrane ADMFCs.
- Water transport through membrane essential for operating anion exchange membrane FC.
- Required water diffusivity for sufficient water supply to cathode is identified.
- Considering the results will help to optimize new membrane material for AFC.

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ABSTRACT

Mathematical modelling is used to analyse water management in Alkaline Direct Methanol Fuel Cells (ADMFCs) with an anion exchange membrane as electrolyte. Cathodic water supply is identified as one of the main challenges and investigated at different operation conditions. Two extreme case scenarios are modelled to study the feasible conditions for sufficient water supply. Scenario 1 reveals that water supply by cathodic inlet is insufficient and, thus, water transport through membrane is essential for ADMFC operation. The second scenario is used to analyse requirements on water transport through the membrane for different operation conditions. These requirements are influenced by current density, evaporation rate, methanol cross-over and electro-osmotic drag of water. Simulations indicate that water supply is mainly challenging for high current densities and demands on high water diffusion are intensified by water drag. Thus, current density might be limited by water transport through membrane. The presented results help to identify important effects and processes in ADMFCs with a polymer electrolyte membrane and to understand these processes. Furthermore, the requirements identified by modelling show the importance of considering water transport through membrane besides conductivity and methanol cross-over especially for designing new membrane materials.

1. Introduction

Recently, alkaline fuel cells (AFCs) attract attention by reason of their ability to operate with non-precious metals as catalyst. Due to higher stability and activity of non-precious metals in alkaline media compared to acidic media, it is possible to use metal catalyst in AFCs other than platinum (Pt), which is commonly used as catalyst in low temperature fuel cells. Replacing Pt catalyst by other metal catalyst can reduce cost of fuel cells and, thus, is the main motivation to improve AFCs. Hence, research regarding AFC mostly focusses on new catalyst materials for oxygen reduction and oxidation of various fuels such as hydrogen, methanol, or other alcohols in alkaline media. A review about new catalyst for AFC can be found in Refs. [1,2].

Alkaline fuel cells are commonly operated using a liquid electrolyte such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) which reacts with dissolved carbon dioxide (CO_2) according to Eq. (2) forming carbonate ions (CO_3^{2-}):

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \quad (1)$$

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$$2K^{+} + CO_3^{2-} \rightarrow K_2CO_3\downarrow \tag{2}$$

On one hand, this carbonation process decreases the performance of the fuel cell due to slower kinetics of fuel oxidation at anode [3] and lower ionic conductivity of the electrolyte [4]. On the other hand carbonates in supersaturated solutions can form precipitating salts (Eq. (2)) that may block pores of gas diffusion layer, catalyst layer or membrane. In order to avoid the disadvantages caused by carbonation of liquid electrolyte, anion exchange membranes were invented as a solid alkaline electrolyte [5]. It has been reported that similar performance of a fuel cell can be obtained with an alkaline anion exchange membrane (AAEM) in CO_3^- form and with the same AAEM in OH^- form [6]. Still, there are only few studies about AFCs using solely a solid electrolyte membrane instead of liquid electrolyte and most of them analyse cell performance for new membranes, ionomers or catalysts [7–11].

It has already been noticed that water transport through membrane might be a limiting factor [11]. Nevertheless, only little attention is given to process engineering issues like water transport through the membrane or water management so far. Diffusion coefficient and electro-osmotic drag coefficient of water through an anion exchange membrane were determined from experimental results by Ref. [12]. Likewise, the water diffusion coefficient through an anion exchange Morgan ADP membrane was estimated from sorption kinetics by Ref. [13]. A model based prediction of the water diffusion coefficient through a SnowPure Excellion I-200 anion exchange membrane is given in Ref. [14] and electro-osmotic water drag coefficients in alkaline media were also determined [15]. Water management has been analysed for AFCs with liquid electrolyte by Refs. [16,17]. These two studies are based on mathematical modelling and belong to the few modelling studies that consider water transport or management in AFCs [16–21]. Although water management in AFCs is even more challenging without liquid electrolyte due to the lack of the buffer function of alkaline solutions, water management has only been studied for the anode of anion exchange membrane fuel cells so far [20,21]. These two studies are using stationary [20] and dynamical [21] 3D modelling to analyse flooding of anode including the influence of changes in various operation conditions. Some modelling works about AFC contain analysis of fuel cell performance [22–26]. The latter is the only modelling study regarding alkaline direct methanol fuel cells (ADMFCs). Furthermore, another two model based studies regarding AFCs without liquid electrolyte were found in literature, both of them analysing the conductivity and water uptake of the AAEM [27,28]. Hence, there is a lack of knowledge and publications in literature regarding modelling and simulation of anion exchange membrane fuel cells, particularly related to water management at cathode and in the whole fuel cell. It is still unclear in which way and intensity water management influences and limits fuel cell performance and what can be done to improve water management and to widen the operation range of the fuel cell. The present study fills that gap by investigating limitation of current density by water management. Requirements on operation conditions and water transport are analysed in order to estimate conditions for stable operation. To our knowledge, this paper presents the first model based analysis of the water management in an ADMFC.

2. Functional principle of an ADMFC

As all fuel cells, ADMFCs convert chemical energy stored in a fuel directly into electric energy using electrochemical reactions. In the case of an ADMFC, methanol is used as fuel which reacts with hydroxide ions (OH^-) in the electrochemical oxidation reaction at the anode producing water and carbon dioxide and releasing electrons:

$$CH_3OH + 6OH^- \rightarrow CO_2\uparrow + 5H_2O + 6e^- \tag{3}$$

At the cathode, OH^--ions are produced in the electrochemical reduction reaction of oxygen:

$$\frac{3}{2}O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \tag{4}$$

Hence, the overall reaction is the same as in acidic direct methanol fuel cells:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \tag{5}$$

During operation, electrons are transported from anode to cathode via an electric circuit whereas OH^--ions are conducted by an electrolyte from cathode to anode.

Since CO_2 is permanently produced at the anode, the carbonation process is more intense in ADMFCs than in alkaline hydrogen fuel cells. Hence, it is important to replace the liquid electrolyte by a solid electrolyte membrane in ADMFCs. A schematic of an ADMFC with a solid electrolyte membrane is shown in Fig. 1. The anode is fed with a methanol water solution while the cathode is flushed with air. Although the reactants are separated by a membrane, some mass transport through the membrane takes place in addition to the ionic transport. Methanol transported through the membrane by diffusion, hereafter named as methanol cross-over, is oxidised at the cathode in a chemical reaction similar to the overall reaction Eq. (5) producing water. This loss of methanol decreases the efficiency of the fuel cell. Furthermore, the methanol oxidation at the cathode causes a decrease in cell potential due to a mixed potential [29]. Similar to methanol, water is also diffusing through the membrane from anode to cathode but

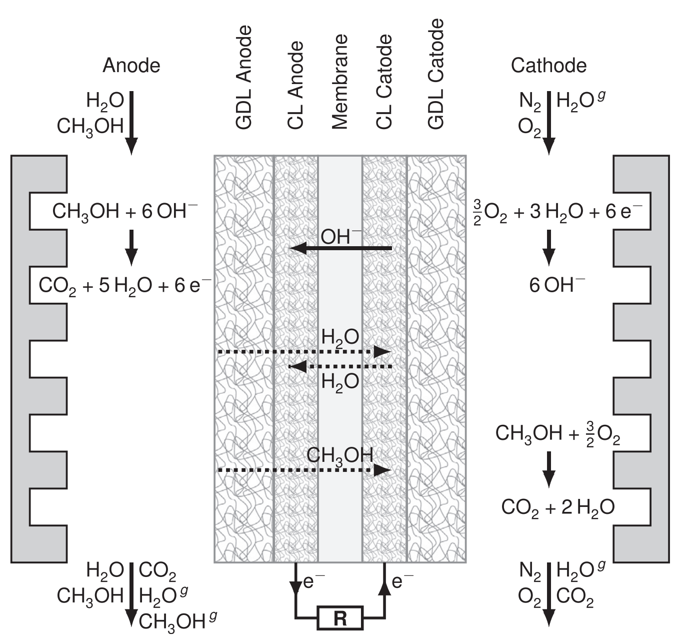

Fig. 1. Schematic of an ADMFC including anode and cathode fluid channels, gas diffusion layers (GDLs), catalyst layers (CLs) and a solid electrolyte membrane.